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On the Basicity of Organic Bases in Different Media

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Table 1. pK_{aH} data for simple nitrogen bases in different media. Most nonobvious structures are depicted in Scheme 1.[a] See the full paper (https://doi.org/10.1002/ejoc.201900956) for references, equations and schemes cited here.

Compound name	CAS Number	pK_{aH}(H_2O)	pK_{aH}(DMSO)	pK_{aH}(MeCN)	pK_{aH}(THF)[b]	GB (kcal mol^{-1})[c]
Primary amines						
$MeNH_2$	74-89-5	10.62[58]	11.0[59]	18.37[34]	13.5±1.8[d]	206.6
$EtNH_2$	75-04-7	10.63[58]	10.9[59]	18.40[34]	13.5±1.8[d]	210
$PrNH_2$	107-10-8	10.53[58]	10.7[59]	18.44[37] [e]	13.8[37]	211.3
i-$PrNH_2$	75-31-0	10.65[58]	10.9±0.4[f]	18.3±0.4[f]		212.5
$BuNH_2$	109-73-9	10.59[58]	11.1[60]	18.26[34]	13.4±1.8[d]	211.9
i-$BuNH_2$	78-81-9	10.42[58]	10.9±0.4[f]	17.92[34]	13.0±1.8[d]	212.9
$BnNH_2$	100-46-9	9.34[58]	10.16[61]	16.92[33] [e]	12.1±1.8[d]	210.2
Aniline	62-53-3	4.62[62]	3.6[60]	10.64[33] [e]	5.2[63]	203.3
NH_3	7664-41-7	9.21[58]	10.5[16]	16.46[34]		195.7
Secondary amines						
Me_2NH	124-40-3	10.64[58]	10.3[59]	19.03 [41]	13.3±1.8[d]	214.3
Et_2NH	109-89-7	10.98[58]	10.5[60]	18.75[34]	13.0±1.8[d]	219.7
Pr_2NH	142-84-7	11.00[58]	10.3±0.5[f]	18.8±0.6[f]		222.1
Bu_2NH	111-92-2	11.25[58]	10.0[60]	18.31[34]	12.6±1.8[d]	223.5
Bn_2NH	103-49-1	8.52[64]				231.3[g]
Ph_2NH	122-39-4	0.79[65]	-1.1±1.2[d]	5.98[33] [e]	0.6±1.8[d]	210.4[g]
N-Me-Aniline	100-61-8	4.85[62]	2.94[66]	10.97[41] [e]	4.8[41]	212.7
Tertiary amines						
Me_3N	75-50-3	9.76[58]	8.4[59]	17.61[34]	12.7±0.5[f]	219.4
Et_3N	121-44-8	10.65[58]	9.0[60]	18.83[33] [e]	12.5[63]	227
Pr_3N	102-69-2	10.65[58]	10.7[67]	18.26[37] [e]	13.0[37]	229.5
Bu_3N	102-82-9	10.89[58]	8.4[60]	18.09[34]	12.7±0.5[f]	231.3
Bn_3N	620-40-6	7.44[68]	4.1[69]	12.9[70]	6.5±1.8[d]	230.4[g]
Ph_3N	603-34-9	-3.91[71]		1.28[42] [e]		209.5
N,N-Dimethylaniline	121-69-7	5.06[62]	2.70[66]	11.47[33] [e]	4.9[63]	217.3
Me_2EtN	598-56-1	9.99[58]	8.5±1.2[d]	18.33[37] [e]	12.6[37]	222.1
$MeEt_2N$	616-39-7	10.29[58]	9±2[f]	18.2±0.9[f]	12.7±0.5[f]	224.7
Et_2PrN	4458-31-5	10.5[72]	9±2[f]	18.2±0.9[f]	12.7±0.5[f]	226.6
Diamines						
NH_2–$(CH_2)_2$–NH_2	107-15-3	9.98[58]	11.1±1.2[d]	18.46[34]	13.6±1.8[d]	218.1
NH_2–$(CH_2)_3$–NH_2	109-76-2	10.47[34]	12.3±1.2[d]	19.76[37] [e]	14.8±1.8[d]	224.7
NH_2–$(CH_2)_4$–NH_2	110-60-1	10.65[34]	12.6±1.2[d]	20.12[34]	15.2±1.8[d]	228.1
NH_2–$(CH_2)_5$–NH_2	462-94-2	10.85[34]	11.7±1.2[d]	19.14[34]	14.2±1.8[d]	226.1
Me_2N–$(CH_2)_2$–NMe_2	110-18-9	9.15[67]	8.8±1.2[d]	18.69[37] [e]	12.8[37]	232.0

Compound name	CAS Number	pK_{aH}(H_2O)	pK_{aH}(DMSO)	pK_{aH}(MeCN)	pK_{aH}(THF)[b]	GB (kcal mol^{-1})[c]
$Me_2N–(CH_2)_3–NMe_2$	110-95-2	10.6[67]	9.4±1.2[d]	19.28[37] [e]	13.0[37]	235.5
$Me_2N–(CH_2)_4–NMe_2$	111-51-3	10.80[67]	10.0±1.2[d]	19.96[37] [e]	13.1[37]	237.3
1,8-$(NH_2)_2$-Naphthalene	479-27-6	4.61[73]		10.99[74]	5.4±1.8[d]	218.0
1,8-$(NMe_2)_2$-Naphthalene	20734-58-1	12.0[75]	7.47[75]	18.63[33] [e]	11.1[63]	238.0
Hydrazine	302-01-2	7.96[34]	10.1[76]	16.61[34]	13.5±1.8[d]	196.6
Cyclic amines						
Piperidine	110-89-4	11.22[58]	10.85[61]	19.35[37] [e]	14.3[37]	220.0
N-Me-piperidine	626-67-5	10.08[58]	8.4±1.2[d]	18.24[37] [e]	12.9[37]	224.7
Piperazine	110-85-0	9.72[64]	10.50[77]	18.69[37] [e]	14.2[37]	218.6
N,N′-Me_2-Piperazine	106-58-1	8.54[67]	7.7±1.2[d]	17.38[37] [e]	12.4[37]	228.8[g]
Pyrrolidine	123-75-1	11.27[58]	11.06[61]	19.62[33] [e]	13.5[63]	218.8
Quinuclidine	100-76-5	11.0[75]	9.8[75]	19.7[78]	13.1±1.8[d]	227.7
DABCO	280-57-9	8.82[75]	9.06[61]	18.29[34]	11.7±1.8[d]	223.4
Bispidine	280-74-0			21.56[37] [e]	14.8±1.8[d]	232.7[g]
Aromatic heterocycles						
Pyridine	110-86-1	5.23[79]	3.4[60]	12.53[33] [e]	5.5[63]	214.7
2,2′-Bipyridine	366-18-7	4.23[80]		12.27[36] [e]		223.1
Quinoline	91-22-5	4.93[79]		11.97[36] [e]		220.2
2,2′-Biquinoline	119-91-5	3.66[67]		11.28[36] [e]		230.0[36] [g]
Isoquinoline	119-65-3	5.46[79]		12.68[36] [e]		219.9
Acridine	260-94-6	5.62[79]		12.66[36] [e]		224.8
Phenanthroline	66-71-7	5.12[81]		13.69[36] [e]		230.9[36] [g]
Imidazole	288-32-4	6.95[82]	6.26[83]	15.07[36] [e]	9.4±1.8[d]	217.3
Benzimidazole	51-17-2	5.56[84]	4.36[83]	13.54[36] [e]		220.0
1,2,3-Triazole	288-36-8	1.17[85]	0.0±1.2[d]	8.0[36] [e]	2.5±1.8[d]	202.5
Benzotriazole	95-14-7	0.42[86]		6.89[36] [e]		210.2[36] [g]
Pyrazole	288-13-1	2.48[85]	1.0±1.2[d]	9.1[36] [e]	3.6±1.8[d]	205.7
Indazole	271-44-3	1.25[87]		7.61[36] [e]		207.7
Pyridazine	289-80-5	2.33[79]	1.8±1.2[d]	10.06[36] [e]	3.7±1.8[d]	209.6
Pyrimidine	289-95-2	1.3[79]	0.55[88]	8.72[36] [e]	2.4±1.8[d]	204.5
Pyrazine	290-37-9	0.6[79]	-0.2±1.2[d]	7.74[36] [e]	1.4±1.8[d]	202.4
Amidines						
DBN	3001-72-7	13.5±1.4[d]	13.4±1.2[d]	23.89[89]	17.2±1.8[d]	240.4
DBU	6674-22-2	13.5±1.5[h]	13.9[90]	24.31[33] [e]	16.9[91]	242.7
TMG	80-70-6	13.0±1.0[h]	13.2[60]	23.35[60] [e]	15.5[92]	238.4
TBD	5807-14-7	15.2±1.0[h]	15.3±1.2[d]	26.02[33] [e]	21.0[92]	244.3
MTBD	84030-20-6	15.0±1.0[h]	14.8±1.2[d]	25.47[33] [e]	18.0[92]	246.2
N,N′-Ph_2-Guanidine	102-06-7	10.02[62]	8.6[93]	17.90[34]	13.9±1.8[d]	236.7[g]
Phosphazenes						
$HP_1(dma)_3$	49778-01-0	15.1±1.0[h]	16.4±1.2[d]	25.85[33] [e]	19.7[92]	249.7[94]
$HP_1(pyrr)_3$	153136-23-3	15.8±1.0[h]	17.4±1.2[d]	27.01[33] [e]	20.8[92]	255.2[94]
t-$BuP_1(dma)_3$	81675-81-2	17.0±1.0[h]	15.7[90]	26.98[33] [e]	18.9[92]	252.9[94]
t-$BuP_1(pyrr)_3$	161118-67-8	17.5±1.0[h]	17.4±1.2[d]	28.42[33] [e]	20.2[92]	258.7[94]
$PhP_1(dma)_3$	35589-04-9	10.64[95]	11.1±1.2[d]	21.26[33] [e]	15.3[63]	246.2[94]
$EtP_2(dma)_5$	165535-45-5	20±2[h]	21.15[90]	32.94[90]	25.3[92]	264.6[94]
t-$BuP_4(dma)_9$	111324-04-0	30±4[h]	30.25[90]	42.7 [h]	33.9[38]	287.7[i]

[a] Where no experimental or reasonably reliable estimated value was available from the literature, the pK_{aH} values were estimated from the data of a few structurally similar compounds or using equations 5-7, whichever was deemed more reliable.

The values were not estimated for compounds of the types underrepresented in the training set or problematic for the corresponding model (see Table 2) and the respective cells are blank. Uncertainty estimates given in the table are with *ca* 90% coverage probability.

[b] The pK_{aH} values in THF refer to free-ion basicities and have been estimated from ion-pair basicities (pK_{ip}) using the Fuoss equation. In original publications[37] these values are termed as pK_{α} to emphasize that they are *estimates* of pK_a (i.e. not directly measured). In this review we do not make distinction between directly measured pK_{aH} values and those that have been estimated from pK_{ip}.

[c] GB values from the NIST Chemistry WebBook database[35] if not stated otherwise.

[d] Estimated with equations 5, 6 or 7.

[e] The reference where the pK_{aH} value was originally published. The values provided here have been re-evaluated and may slightly differ from the primary source. See the text for the discussion on the uncertainty of the values.

[f] Average pK_{aH} values of the aliphatic amines (bar benzylamines) with the same number of substituents.

[g] Calculated with G4MP2 method

[h] Recommended pK_{aH} values from ref [96] (in water) or ref [90] (in MeCN). Most of these values are not experimental but obtained by combining information from experiments, computations and/or correlation analysis. Some on these values may not be experimentally observable due to the properties of the specific solvents.

[i] Calculated value (DFT BP TZVP) from ref [2].